(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 660 192 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
06.11.2013 Bulletin 2013/45

(21) Application number: **10861263.1**

(22) Date of filing: **30.12.2010**

(51) Int Cl.:
B82B 3/00 *(2006.01)* ***C01B 31/02*** *(2006.01)*

(86) International application number:
PCT/CN2010/080531

(87) International publication number:
WO 2012/088697 (05.07.2012 Gazette 2012/27)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

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(54) GRAPHENE RAMIFICATION-CARBON NANOTUBE COMPOSITE MATERIAL AND PREPARATION METHOD THEREOF

(57) A graphene ramification-carbon nanotube composite material and preparation method thereof which includes the following steps: step one, adding the graphene ramification and carbon nanotubes to alcohol dispersant and dispersing for 120 - 150 minutes by ultrasonic to form a stable suspension; step two, filtrating the suspension, drying the solid substance and cooling it to room temperature to obtain the graphene ramification-carbon nanotube composite material. In the composite material produced by the method, the graphene ramification and carbon nanotube composite form an intermixing and interveining structure to avoid the aggregation and stacking of the graphene ramification, so as to enable complementarities in structure and function of the graphene ramification and carbon nanotubes and improve the conductive property of the composite material.

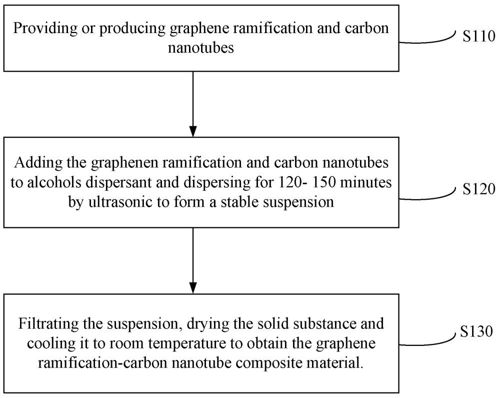

FIG. 1

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a field of nano-carbon composite material, and more particularly relates to a graphene derivative-carbon nanotube composite material and a preparation method thereof.

BACKGROUND OF THE INVENTION

[0002] A graphene material was prepared by Andre K. Geim, et al at the university of Manchester in England in 2004, the graphene material was received a widespread attention because of its unique structure and optoelectronic properties. Monolayer graphite is considered to be an ideal material due to its large specific surface area, excellent electrical conductivity, excellent thermal conductivity and low thermal expansion coefficient. For example, it has: 1, a high-strength, Young's modulus (1,100 GPa), breaking strength (125GPa); 2, a high thermal conductivity, (5,000W/mK); 3, a high conductivity, and carrier transport rate, (200,000 $cm^2/V*s$); 4, a high specific surface area, (theoretical calculated value: 2,630m^2/g). It can be used as an electrode material in the super-capacitor and the lithium ion battery especially for its high electrical conductivity properties, the large specific surface and a single molecular layer of the two-dimensional nano-scale structures.

[0003] Carbon nanotube was found in the carbon fibers produced by the arc discharge method in the 1991. (S. Iijima, Nature, 354, 56 (1991)). Carbon nanotube is a type of tubular carbon molecule, each carbon atom in the tube is taken Sp^2 hybridized and connected by carbon to carbon bond, the hexagonal honeycomb structure is formed as a skeleton of the carbon nanotube; the length-to-diameter ratio of carbon nanotube is above 1000:1, the intensity ratio is more than 100 times greater than the steel in the same volume , but the weight is 1/6 to 1/7 of the latter one; the hardness is equal to the diamond, but it has a good flexibility, it is an ideal fiber material with a high strength, and so it is called a "super fiber".

[0004] In the field of nano carbon composite structures, most researches have been focusing on the combination of metal particles, organic molecule with the carbon nanotube or graphene. It is equivalent to a research of the doping of one-dimensional and zero-dimensional carbon material. The complex of the carbon-based material is mainly concentrated in the process of growing the carbon nanotube, while other carbon allotropes are produced. The widely research includes a zero-dimensional and one-dimensional composite structure--Nano peapods found in 1998, (Smith, g.W. et al. Nature396, 323 (1998)). Fujitsu Laboratories published the success of synthesizing a new nano carbon composite structure formed by self-organizing of carbon nanotube and graphene nano-carbon in the 34th Fullerene Nanotubes General Symposiun in March 2008. Fujitsu Laboratories used chemical vapor deposition method to form a composite structure the composite structure was formed by self-organization of several to dozens of layers of graphite, which was generated in order on the backplane perpendicular direction of multi-walled carbon nanotube at a temperature of 510°C. It was the first time to implement vertical engaging of non-atomic structure of the bonded structure of the one-dimensional structure of the carbon nanotubes and a two-dimensional structure of the graphene.

[0005] However, the conductive properties of the conventional composite material of graphene - carbon nanotube still need to be further improved.

SUMMARY OF THE INVENTION

[0006] According to the above problems, one object of the present invention is to provide a graphene derivative-carbon nanotube composite material and a preparation method thereof.

[0007] A graphene derivative-carbon nanotube composite material, containing a graphene derivative and a carbon nanotube with a mass ratio of 1~5:1, the graphene derivative and the carbon nanotube in the graphene derivative-carbon nanotube composite material interpenetrate and intertwine to each other to form a connected network structure.

[0008] In a preferred embodiment, the graphene derivative is fluorinated graphene oxide or nitrogen-doped graphene oxide.

[0009] In a preferred embodiment, the carbon nanotube is a hollow tubular carbon material having a diameter of 5nm to 200nm and a length of 0.1 μm to 100μm.

[0010] A preparation method of a graphene derivative-carbon nanotube composite material includes the following steps:

[0011] step one, adding a graphene derivative and a carbon nanotube to an alcohol dispersant and ultrasonic dispersing for 120 minutes to 150 minutes to obtain a stable suspension; and

[0012] step two, filtrating the suspension to obtain a solid, drying and cooling the solid to a room temperature to obtain the graphene derivative-carbon nanotube composite material.

[0013] In a preferred embodiment, a mass ratio of the graphene derivative and the carbon nanotube in the step one is 1~5:1.

[0014] In a preferred embodiment, the alcohol dispersant in the step one is selected from the group consisting of ethanol, ethylene glycol and isopropanol.

[0015] In a preferred embodiment, a drying temperature in the step two is 50°C to 80°C, and a drying time in the step two is 48 hours to 56 hours.

[0016] In a preferred embodiment, the graphene derivative in the step one is fluorinated graphene oxide or nitrogen-doped graphene oxide.

[0017] In a preferred embodiment, the fluorinated graphene oxide is prepared by the following method:

[0018] preparing graphene oxide by using graphite; and

[0019] performing a reaction between the graphene oxide and a mixed gas containing N_2 and F_2 for 0.5 hour to 24 hours at a temperature from 20°C to 200°C, and obtaining the fluorinated graphene oxide.

[0020] In a preferred embodiment, the nitrogen- doped graphene oxide is prepared by the following method:

[0021] preparing graphene oxide by using graphite; and

[0022] heating the graphene oxide under the atmosphere of ammonia, at a temperature from 500°C to 800°C with a rate of 10°C/min, then heat preserving for 2 hours, cooling to a room temperature to obtain the nitrogen-doped graphene oxide.

[0023] In the composite material, the graphene derivative and carbon nanotube composite form an intermixing and interveining structure to prevent the aggregation and stacking of the graphene derivative, so as to enable complementarities in structure and function of the graphene derivative and carbon nanotubes and improve the conductive property of the composite material.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] The preferred embodiments of the present invention are described more specifically by the drawings, the objects, features and advantages of the present invention and others will become much clear. The same figures indicate the same portions in all the drawings. The drawing do not draw scaling in proportion to the actual size deliberately, it is focused on showing the gist of the present invention.

[0025] FIG. 1 is a flowchart of preparation method of the graphene derivative-carbon nanotube composite material according to one embodiment of the present invention;

[0026] FIG. 2 shows a scanning electron microsope image of the carbon nanotube according to one embodiment of the present invention;

[0027] FIG. 3 shows a scanning electron microsope image of the fluorinated graphene oxide according to one embodiment of the present invention;

[0028] FIG. 4 shows a scanning electron microsope image of the fluorinated graphene oxide -carbon nanotube composite material according to one embodiment of the present invention;

[0029] FIG. 5 shows a scanning electron microsope image of the nitrogen-doped graphene oxide according to one embodiment of the present invention;

[0030] FIG. 6 shows a scanning electron microsope image of the nitrogen-doped graphene oxide-carbon nanotube composite material according to one embodiment of the present invention.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0031] For a better understanding of the objects, features and advantages of the present invention, the following examples and drawings are provided to further illustrate the technical solutions of the present invention. Numerous specific details are described in the following description in order to fully understand the present invention. A lot different ways can also implement besides the describing in the present invention, it is apparent to those skilled in the art that a variety of modifications and changes may be made without departing from the scope of the present invention .the scope of the present invention is not limited to the following examples.

[0032] A graphene derivative-carbon nanotube composite material includes a graphene derivative and a carbon nanotube with a mass ratio of 1~5:1, the graphene derivative and the carbon nanotube in the graphene derivative-carbon nanotube composite material interpenetrate and intertwine to each other to form a connected network structure.

[0033] The two-dimensional structure of the single molecular layer of the graphene derivative may easily be agglomerated, laminated, curled or highly wrinkled in the drying process for removing the interlayer water, which may lead to a great reduction of the utilization rate of the specific surface area. Since there are many similarities in structure and performance of carbon nanotube and graphene derivative, the carbon nanotube can be inserted to layers of the graphene derivative, or the functional groups on the carbon nanotube and the graphene derivative can react with each other, such that the carbon nanotube is grafted in the surface of the graphene derivative, and layers of the graphene are separated from each other, the specific surface area of the graphene derivative after drying is improved, the agglomeration and lamination of the graphene derivative is avoided, thereby the specific capacitance of supercapacitor is increased.

[0034] The graphene derivative may be fluorinated graphene oxide or nitrogen-doped graphene oxide. The carbon nanotube may be a hollow tubular carbon material having a diameter of 5nm to 200nm and a length of 0.1 μm to 100μm. As the electrode material, the discharge capacity of the fluorinated graphite oxide is greatly improved comparing to the graphite oxide. The discharge capacity is 675mAh/g and the energy density is 1420Wh/Kg when the discharge current density is 0.5mA/cm^2 (1M $LiClO_4$-PC). N-doped graphene oxide is generated when the graphene oxide is doped by nitrogen, not only its stability can be improved, but also the conductivity performance can be enhanced, and a clear biological n-type effect is appeared.

[0035] Referring to FIG. 1, a preparation method of the graphene derivative-carbon nanotube composite material includes the following steps:

[0036] Step S110, the graphene derivative and carbon nanotube are provided or prepared.

[0037] The graphene derivative may be fluorinated graphene oxide or nitrogen-doped graphene oxide.

[0038] The fluorinated graphene oxide may be prepared by the conventional methods. Preferably, it may be prepared by the following method:

[0039] Step S111, a graphene oxide is prepared by using graphite.

[0040] (a), graphite, potassium persulfate, and phosphorus pentoxide are added to concentrated sulfuric acid at a temperature of 80°C to 120°C with a mass ratio of 2~10:1:1, the mixture is naturally cooled after uniformly stirred, then the mixture is washed to neutral and dried to obtain a mixture. The graphite is preferable flake graphite.

[0041] (b), The mixture and a potassium permanganate are added to concentrated sulfuric acid, the temperature of the mixed solution is maintained at a temperature from 15°C to 20°C, and then maintained for 1 hours to 3 hours in the oil bath at a temperature from 25°C to 35°C, the deionized water and the hydrogen peroxide solution are added to have a reaction, filtrated, a solid was collected.

[0042] (c), the solid is washed by diluted hydrochloric acid, and dried to obtain the graphene oxide.

[0043] (d), the graphene oxide is added to the deionized water and ultrasound vibrated for 1 hour to obtain a uniform dispersion of graphene oxide colloidal solution, then the graphene oxide colloidal solution is filtered and a solid is collected , then the solid is vacuum dried to obtain the graphene oxide.

[0044] Step S112, the graphene oxide and a mixed gas containing N_2 and F_2 are reacted for 0.5 hour to 24 hours at a temperature from 20°C to 200°C, the fluorinated graphene oxide is obtained.

[0045] Preferably, the graphene oxide obtained from the S111 is placed in the reactor, the mixed gas containing N_2 and F_2 is introduced (a volume fraction of F_2 is 5% to 30%), the mixture is heated and the temperature is maintained at a temperature from 20°C to 200°C, the reaction is lasted for 0.5 hour to 24 hours, such that the graphene oxide and F_2 are reacted, F is partially substituted by O, the fluorinated graphene oxide is obtained.

[0046] In a more preferred embodiment, the volume fraction of F_2 in the mixed gas is 10%, the reaction temperature is 100°C, the reaction time is 1 hour.

[0047] The nitrogen-doped graphene oxide may be prepared by the conventional methods. Preferably, itmay be prepared by the following method:

[0048] Step S111', a graphene oxide is prepared by using graphite.

[0049] The process of the step is substantially the same as step S111.

[0050] Step S112', the graphene oxide obtained from the step S111' is placed under the atmosphere of ammonia, the graphene oxide is heated to a temperature from 500°C to 800°C with a rate of 10°C/min, heat preserved for 2 hours, the reaction product is cooled to a room temperature to obtain the nitrogen-doped graphene oxide.

[0051] Preferably, the sample of the graphene oxide is placed in a heating furnace and a high-purity ammonia is introduced, the flow rate of ammonia is controlled at a rate of 80mL/min, and the time for introducing ammonia is 5 minutes to 10 minutes to replace the air in the tube furnace, and then the furnace is heated to the reaction temperature from 500°C to 800°C with a rate of 10°C/min, the temperature is maintained for 2 hours. After the reaction is ended, the reaction product was cooled under an ammonia atmosphere to a room temperature to obtain the nitrogen-doped graphene oxide.

[0052] The carbon nanotube may be prepared by the traditional methods. Preferably, the carbon nanotube is a hollow tubular carbon material having a diameter of 5nm to 200nm and a length of 0.1μm to 100μm.

[0053] Step S120, the graphene derivative obtained and a carbon nanotube from the step S110 are added to an alcohol dispersant and ultrasonic dispersed to obtain a stable suspension.

[0054] Preferably, the graphene derivative and the carbon nanotube are added to alcohol dispersant with a mass ratio of 1~5:1, and ultrasonic dispersed for 120 minutes to 150 minutes to obtain a stable suspension.

[0055] The alcohol dispersant is preferable selected from the group consisting of ethanol, ethylene glycol and isopropanol.

[0056] Step S 130, the suspension is filtrated to obtain a solid, the solid is dried and cooled to a room temperature to obtain the graphene derivative-carbon nanotube composite material.

[0057] Preferably, the solid is vacuum dried for 48 hours to 56 hours at a temperature from 50°C to 80°C, then cooled to a room temperature to obtain the graphene derivative-carbon nanotube composite material.

[0058] The preparation method has the following advantages:

[0059] (1) The graphene oxide doped with fluorine or nitrogen is simply prepared with the graphene oxide, which improves the stability of the graphene oxide.

[0060] (2) The oxygen atom is substituted; the capacity of the electrode material can be significantly improved by doping with fluorine or nitrogen. The charge specific capacity of super-capacitor prepared of the graphene derivative-carbon nanotube composite material is 99F/g~112F/g, the discharge specific capacity is 96F/g~110F/g, the charge-discharge efficiency is 97%~99.5%.

[0061] (3) In the composite material, the graphene derivative and carbon nanotube composite form an intermixing and interveining structure to avoid the aggregation and stacking of the graphene derivative, so as to enable complementarities in structure and function of the graphene derivative and carbon nanotubes and improve the conductive property of the composite material.

[0062] The following examples are provided for further illustration. All the reagents are of analytical grade.

[0063] EXAMPLE 1

[0064] (1) A natural flake graphite having a purity of 99.5% was provided.

[0065] (2) The graphite oxide was prepared according to the modified Hummers method. The specific steps were: 20g 50 mesh of graphite powder, 10g of potassium persulfate and 10g of phosphorus pentoxide were added to concentrated sulfuric acid at a temperature of 80°C, and the mixture was stirred uniformly, cooled for more than 6 hours, washed to neutral and dried to obtain a sample. The dried sample was added to 230mL of concentrated sulfuric acid at a temperature of 0°C, then 60g of potassium permanganate was added, the temperature of the mixture was maintained for 30 minutes below 20°C, and then maintained in the oil bath at a temperature of 35°C for 2 hours, 920mL of deionized water was slowly added. 15 minutes later, 2.8L of deionized water (containing 50mL of hydrogen peroxide with a concentration of 30%) was then added, the mixture was hot filtrated while the color of the mixture became bright yellow, and then washed with 5L of hydrochloric acid with a concentration of 10%, filtrated, and vacuum dried for 48 hours at a temperature of 60°C to obtain the graphite oxide.

[0066] (3) 20 g of graphite oxide and 200 mL of deionized water were added to a beaker to form a mixture, the mixture was ultrasonic dispersed for 1 hour, a claybank homogeneous transparent solution was obtained, and a colloidal solution with uniformly dispersed graphene oxide was formed, filtrated, and vacuum dried for 48 hours at a temperature of 60°C to obtain the graphene oxide.

[0067] (4) The dried graphene oxide was loaded into a reactor, and a dry nitrogen was introduced for 4 hours, and then the fluorine was introduced to react with the graphene oxide for 1 hour at a temperature of 100°C to obtain the fluorinated graphene oxide. The volume fraction of the fluorine in the mixed gas was 10%.

[0068] (5) 100mg of the fluorinated graphene oxide and 100mg of the carbon nanotube were added to 500 mL of ethanol to form a mixture, a diameter of the carbon nanotube was 5 nm, a length of the carbon nanotube was 0.1 μm, the mixture was ultrasonic dispersed for 120 minutes such that both the fluorinated graphene oxide and the carbon nanotube were uniformly dispersed, and a stable suspension was obtained. The suspension was filtered, and vacuum dried for 48 hours at a temperature of 50°C, the fluorinated graphene oxide - carbon nanotube composites material was obtained.

[0069] Referring to FIG. 2, FIG. 2 shown a scanning electron microsope (SEM) image of the carbon nanotube of example 1. Referring to FIG. 3, FIG. 3 shown a scanning electron microsope (SEM) image of the fluorinated graphene oxide of example 1. Referring to FIG. 4, FIG. 4 shown a scanning electron microsope (SEM) image of the fluorinated graphene oxide -carbon nanotube composite material of example 1. It may be seen from FIG 2 to FIG 4 that, there was a phenomenon of agglomeration in a single carbon nanotube or a single fluorinated graphene oxide, while the fluorinated graphene oxide was isolated uniformly by the carbon nanotube in the fluorinated graphene oxide -carbon nanotube composite material, the phenomenon of laminate or agglomeration did not occur.

[0070] EXAMPLE 2

[0071] (1) A natural flake graphite having a purity of 99.5% was provided.

[0072] (2) The graphite oxide was prepared according to the modified Hummers method. The specific steps were: 20g 50 mesh of graphite powder, 10g of potassium persulfate and 10g of phosphorus pentoxide were added to concentrated sulfuric acid at a temperature of 80°C, and the mixture was stirred uniformly, cooled for more than 6 hours, washed to neutral and dried to obtain a sample. The dried sample was added to 230mL of concentrated sulfuric acid at a temperature of 0°C, then 60g of potassium permanganate was added, the temperature of the mixture was maintained for 30 minutes below 20°C, and then maintained in the oil bath at a temperature of 35°C for 2 hours, 920mL of deionized water was slowly added. 15 minutes later, 2.8L of deionized water (containing 50mL of hydrogen peroxide with a concentration of 30%) was then added, the mixture was hot filtrated while the color of the mixture became bright yellow, and then washed with 5L of hydrochloric acid with a concentration of 10%, filtrated, and vacuum dried for 48 hours at a temperature of 60°C to obtain the graphite oxide.

[0073] (3) 20 g of graphite oxide and 200 mL of deionized water were added to a beaker to form a mixture, the mixture was ultrasonic dispersed for 1 hour, a claybank homogeneous transparent solution was obtained, and a colloidal solution with uniformly dispersed graphene oxide was formed, filtrated, and vacuum dried for 48 hours at a temperature of 60°C to obtain the graphene oxide.

[0074] (4) The graphene oxide was loaded into a tube of furnace, and a high purity ammonia was introduced, the flow rate of ammonia was controlled by a gas-flowmeter, the flow rate of ammonia was controlled at a rate of 80mL/min, and the ammonia was introduced for 10 minutes to replace air in the tube furnace, and then the furnace was heated, the temperature was raised to a reaction temperature of 800°C at a rate of 10°C/min, maintained for 2 hours. After the reaction was ended, the reaction product was cooled to room temperature under the ammonia atmosphere, and then the nitrogen-doped graphene oxide was removed from the furnace after the reaction.

[0075] (5) 200mg of the nitrogen-doped graphene oxide and 100mg of the carbon nanotube were added to 500 mL of ethylene glycol, a diameter of the carbon nanotube was 200 nm, a length of the carbon nanotube was 100 μm, the mixture was ultrasonic dispersed for 150 minutes such that both the nitrogen-doped graphene oxide and the carbon nanotube were uniformly dispersed, and a stable suspension was obtained. The suspension was filtered, and vacuum dried for 48 hours at a temperature of 50°C, the nitrogen-doped graphene oxide - carbon nanotube composites material was obtained.

[0076] Referring to FIG. 5, FIG. 5 shown a scanning electron microsope (SEM) image of the nitrogen-doped graphene oxide of example 2. It may be seen from FIG 5 that, the nitrogen-doped graphene oxide was agglomerated and wrinkled. Referring to FIG. 6, FIG. 6 shown a scanning electron microsope (SEM) image of the nitrogen-doped graphene oxide -carbon nanotube composite material of example 2. It may be seen from FIG 6 that, the nitrogen-doped graphene oxide was isolated uniformly by the carbon nanotube in the nitrogen-doped graphene oxide -carbon nanotube composite material, the phenomenon of laminate or agglomeration did not occur.

[0077] EXAMPLE 3

[0078] Fluorinated graphene oxide was prepared according to the example 1;

[0079] 300mg of the fluorinated graphene oxide and 100mg of the carbon nanotube were added to 500 mL of ethanol, a diameter of the carbon nanotube was 50 nm, a length of the carbon nanotube was 30 μm, the mixture was ultrasonic dispersed for 120 min such that both the fluorinated graphene oxide and the carbon nanotube were uniformly dispersed, and a stable suspension was obtained. The suspension was filtered, and vacuum dried at a temperature of 80°C for 56 hours, the graphene derivative-carbon nanotube composite material was obtained.

[0080] EXAMPLE 4

[0081] The nitrogen-doped graphene oxide was prepared according to the example 2;

[0082] 500mg of the nitrogen-doped graphene oxide and 100mg of the carbon nanotube were added to 500 mL of ethylene glycol to form a mixture, a diameter of the carbon nanotube was 100nm, a length of the carbon nanotube was 50μm, the mixture was ultrasonic dispersed for 150 minutes such that both the nitrogen-doped graphene oxide and the carbon nanotube were uniformly dispersed, and a stable suspension was obtained. The suspension was filtered, and vacuum dried at a temperature of 60°C for 50 hours, the nitrogen-doped graphene oxide - carbon nanotube composites material was obtained.

[0083] The graphene derivative - carbon nanotube composites material obtained from example 1 to 4 were used as electrode material of super-capacitor, the charge-discharge capacity and charge-discharge efficiency of the super capacitor were shown in table 1.

Table 1 the charge-discharge specific capacity and charge-discharge efficiency of the super capacitor

example	charge specific capacity(F/g)	discharge specific capacity(F/g)	charge-discharge efficiency
Example 1	110.48	108.32	98.04%
Example 2	99.56	96.69	97.12%
Example 3	106.63	103.98	97.51%
Example 4	103.54	101.29	95.83%

[0084] It may be seen from Table 1 that, the super-capacitor prepared of graphene derivative-carbon nanotube composite material according to the examples had a high charge and discharge specific capacity and a high charge-discharge efficiency.

[0085] It should be understood that the descriptions of the examples are specific and detailed, but those descriptions can't be used to limit the present disclosure. Therefore, the scope of protection of the invention patent should be subject to the appended claims. It should be noted that it is apparent to those skilled in the art that a variety of modifications and changes may be made without departing from the conception of the present invention, those belongs to the scope of the present invention. So the scope of the present invention is intended to be defined by the appended claims.

Claims

1. A graphene derivative-carbon nanotube composite material, comprising a graphene derivative and a carbon nanotube with a mass ratio of 1~5:1, the graphene derivative and the carbon nanotube in the graphene derivative-carbon nanotube composite material interpenetrate and intertwine to each other to form a connected network structure.

2. The graphene derivative-carbon nanotube composite material according to claim 1, wherein the graphene derivative is fluorinated graphene oxide or nitrogen-doped graphene oxide.

3. The graphene derivative-carbon nanotube composite material according to claim 1, the carbon nanotube is a hollow tubular carbon material having a diameter of 5nm to 200nm and a length of 0.1 μm to 100μm.

4. A preparation method of a graphene derivative-carbon nanotube composite material, comprising the following steps:

   step one, adding graphene derivative and carbon nanotube to an alcohol dispersant and ultrasonic dispersing for 120 minutes to 150 minutes to obtain a stable suspension; and
   step two, filtrating the suspension to obtain a solid, drying and cooling the solid to a room temperature to obtain the graphene derivative-carbon nanotube composite material.

5. The preparation method of claim 1, wherein a mass ratio of the graphene derivative and the carbon nanotube in the step one is 1~5:1.

6. The preparation method of claim 1, wherein the alcohol dispersant in the step one is selected from the group consisting of ethanol, ethylene glycol and isopropanol.

7. The preparation method of claim 1, wherein a drying temperature in the step two is 50°C to 80°C, and a drying time in the step two is 48 hours to 56 hours.

8. The preparation method of claim 1, wherein the graphene derivative in the step one is fluorinated graphene oxide or nitrogen-doped graphene oxide.

9. The preparation method of claim 8, wherein the fluorinated graphene oxide is prepared by the following method:

   preparing graphene oxide by using graphite; and
   performing a reaction between the graphene oxide and a mixed gas containing N_2 and F_2 for 0.5 hour to 24 hours at a temperature from 20°C to 200°C, and obtaining the fluorinated graphene oxide.

10. The preparation method of claim 8, wherein the nitrogen-doped graphene oxide is prepared by the following method:

    preparing graphene oxide by using graphite; and
    heating the graphene oxide under the atmosphere of ammonia at a temperature from 500° to 800°C with a rate of 10°C/min, then heat preserving for 2 hours, cooling to a room temperature to obtain the nitrogen-doped graphene oxide.

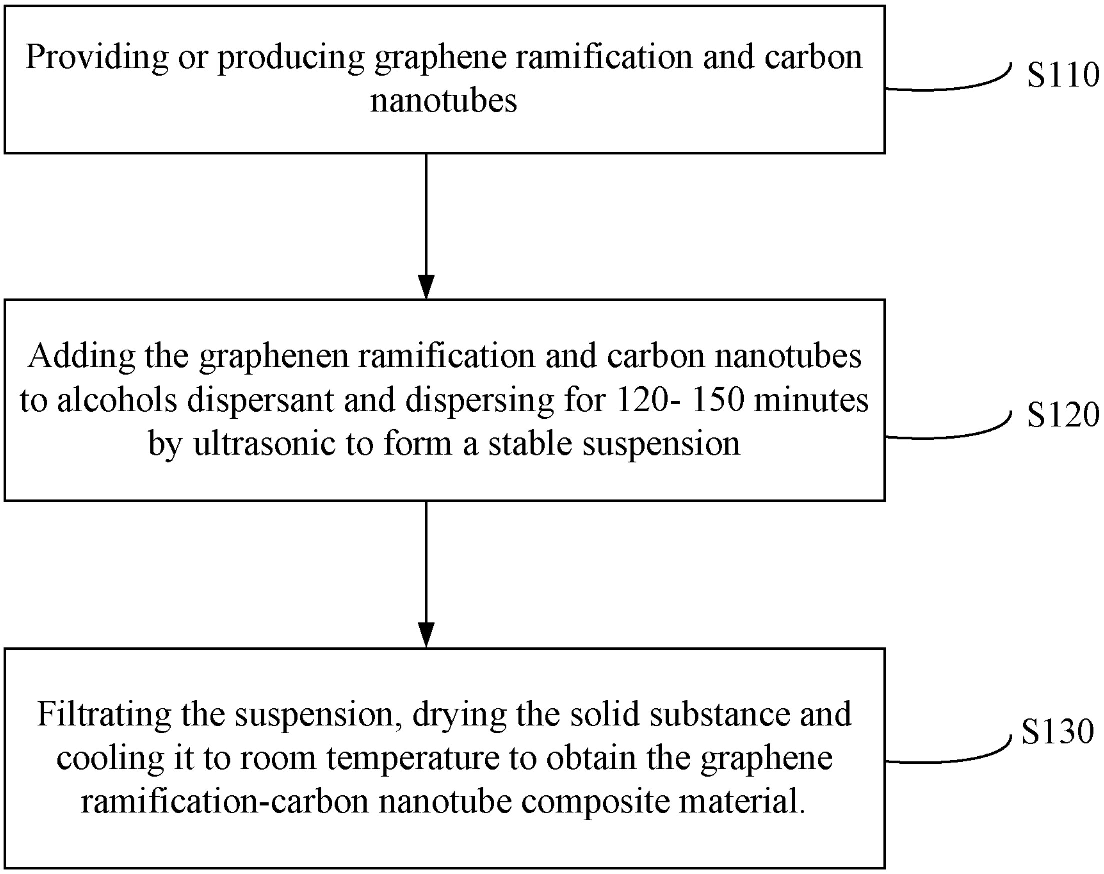
Providing or producing graphene ramification and carbon nanotubes
S110
Adding the graphenen ramification and carbon nanotubes to alcohols dispersant and dispersing for 120- 150 minutes by ultrasonic to form a stable suspension
S120
Filtrating the suspension, drying the solid substance and cooling it to room temperature to obtain the graphene ramification-carbon nanotube composite material.
S130

FIG. 1

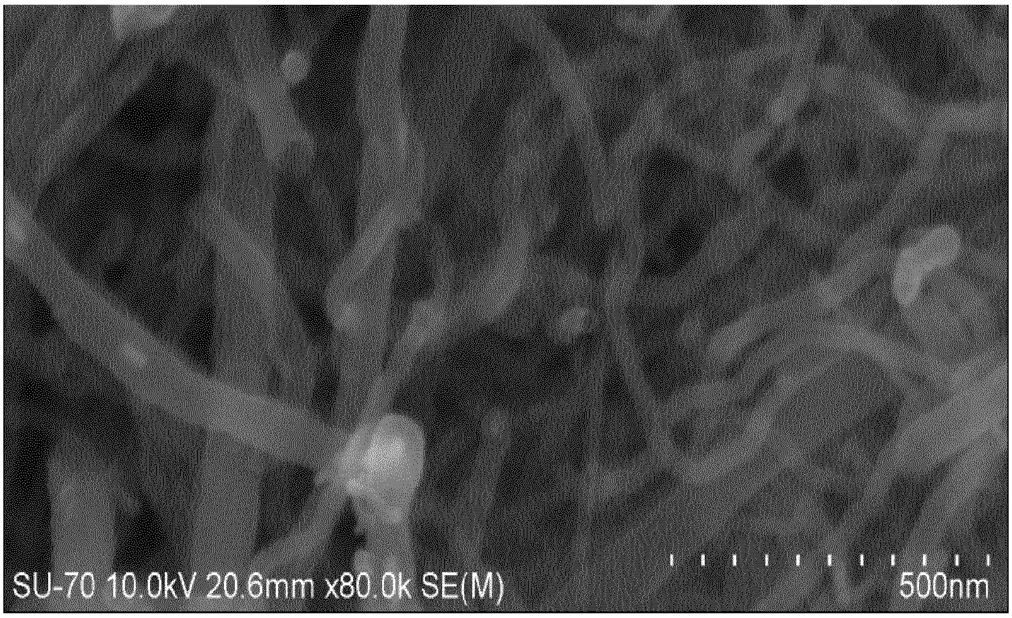

FIG. 2

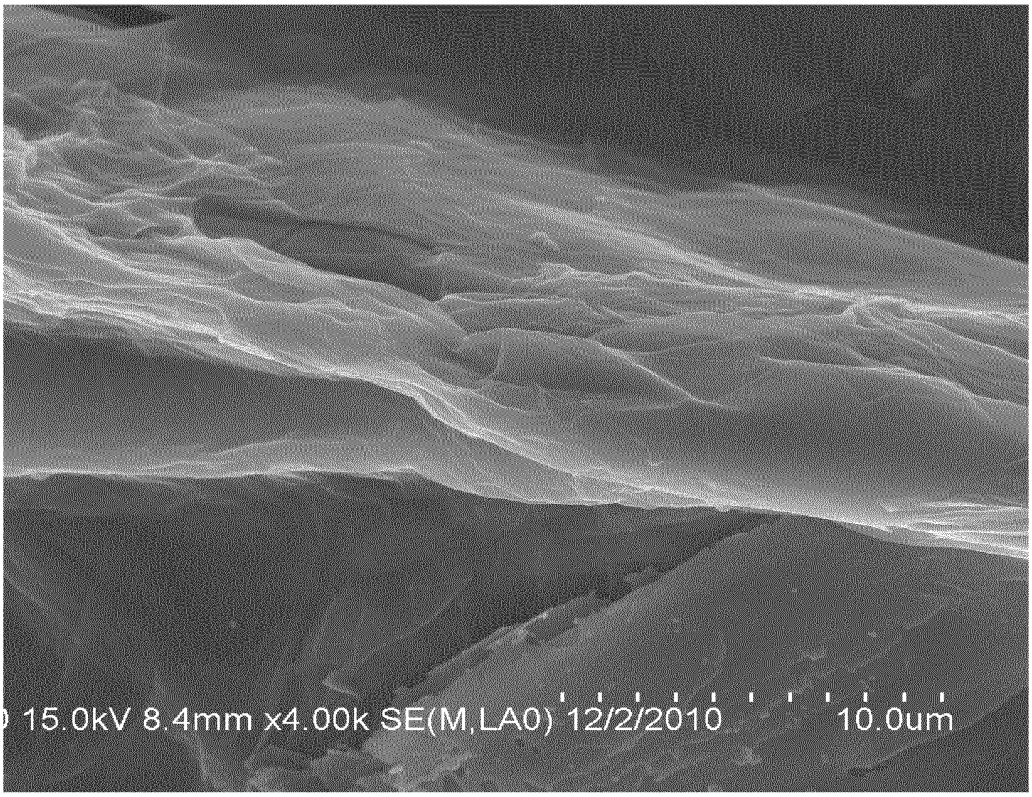

FIG. 3

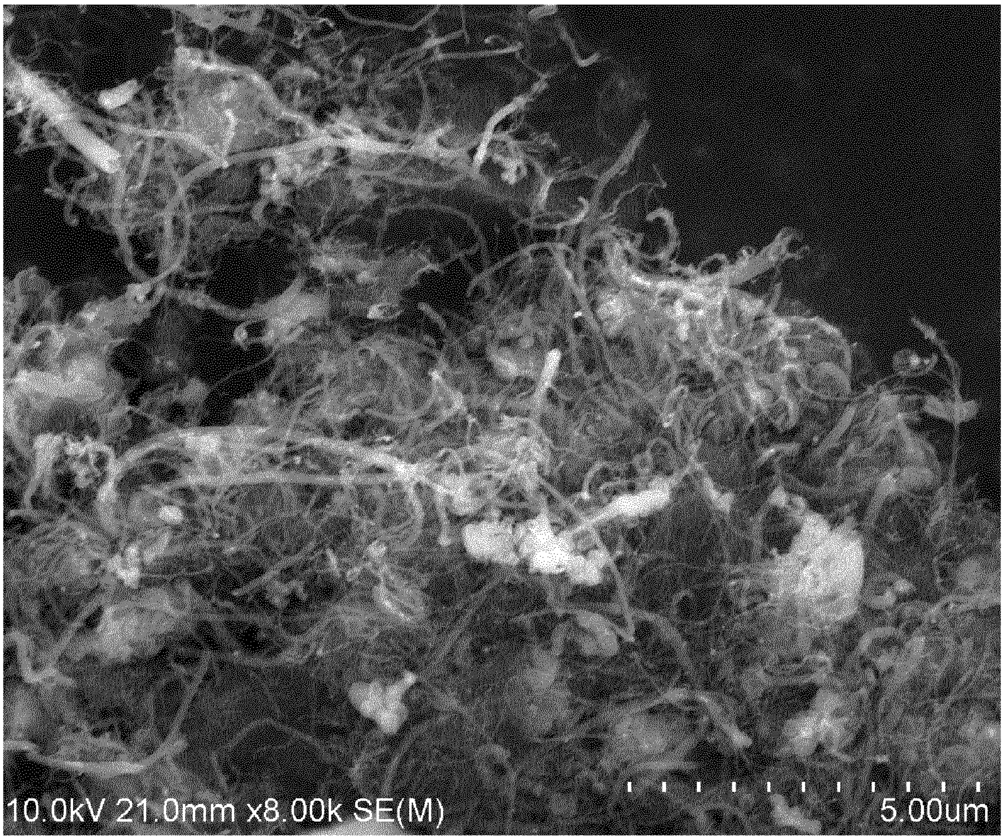

FIG. 4

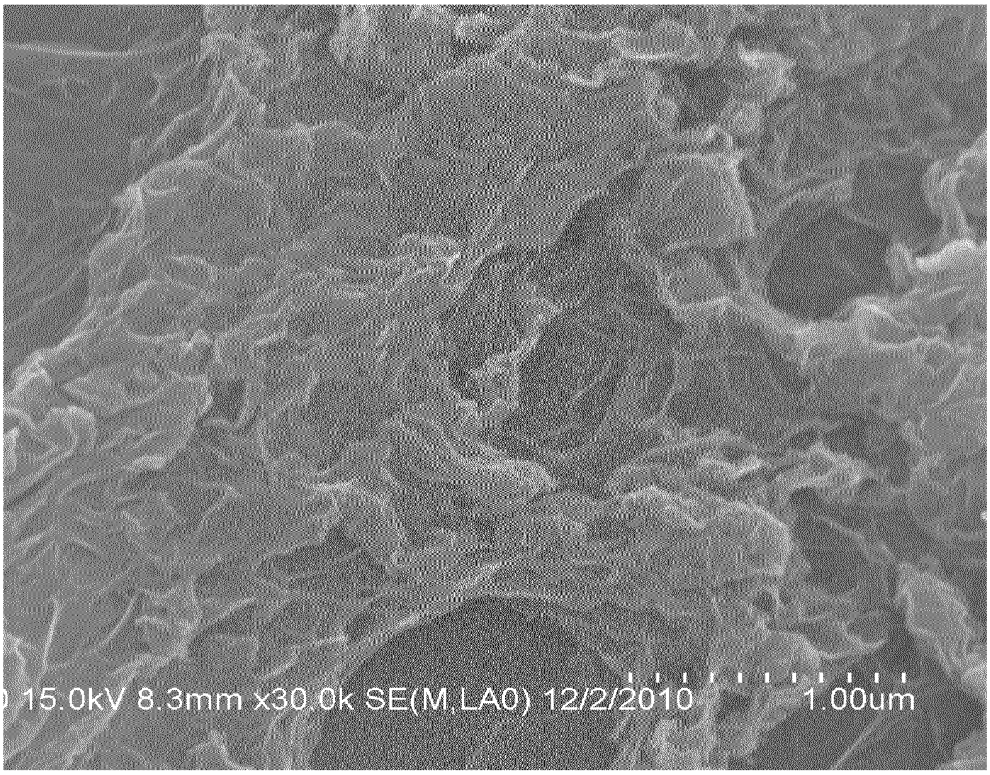

FIG. 5

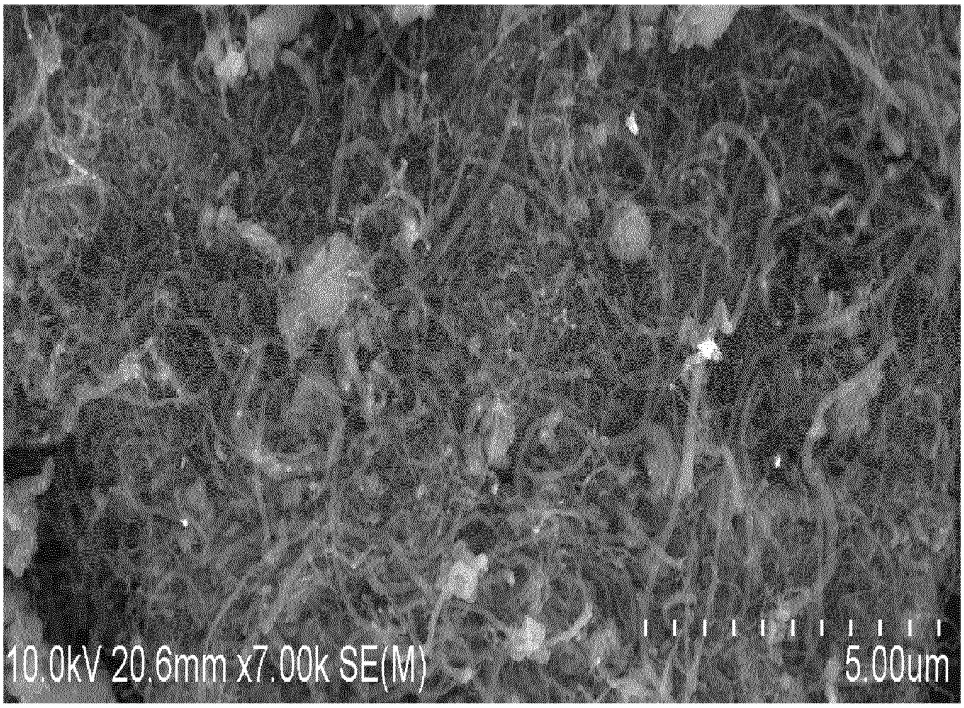

FIG. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2010/080531

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC：B82B，C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CPRS，VEN，DWPI，CNABS，CNKI praphene, carbon+, nano+, tube?, oxid+, suspend+, conduct+, electric, compsite

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN101734650A（UNIV SHENYANG ARCHITECTURAL）16 Jun. 2010（16.06.2010） the description pages 2-3	1-10
A	CN101712452A（UNIV HARBIN ENG）26 May 2010（26.05.2010） the whole document	1-10
A	CN101811690A（NAT CENT NANOSCIENCE&TECHNOLOGY CHINA） 25 Aug. 2010（25.08.2010）the whole document	1-10
A	CN101575095A（UNIV BEIJING）11 Nov. 2009（11.11.2009）the whole document	1-10
A	US2008206124A1（JANG, BOR Z et al）28 Aug. 2008（28.08.2008） the whole document	1-10

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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Date of the actual completion of the international search 27 Sept. 2011（27.09.2011）	Date of mailing of the international search report **20 Oct. 2011 (20.10.2011)**
Name and mailing address of the ISA/CN The State Intellectual Property Office, the P.R.China 6 Xitucheng Rd., Jimen Bridge, Haidian District, Beijing, China 100088 Facsimile No. 86-10-62019451	Authorized officer YANG,Yan Telephone No. (86-10)62085559

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2010/080531

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CN101734650A	16.06.2010	None	
CN101712452A	26.05.2010	None	
CN101811690A	25.08.2010	None	
CN101575095A	11.11.2009	None	
US2008206124A1	28.08.2008	US7892514 B2	22.02.2011

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2010/080531

A. CLASSIFICATION OF SUBJECT MATTER

B82B3/00(2006.01)i
C01B31/02(2006.01)i

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REFERENCES CITED IN THE DESCRIPTION

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- **SMITH, G.W. et al.** *Nature,* 1998, vol. 396, 323 **[0004]**